SOLVOTHERMAL PREPARATION OF Mg-MOF-74 IN A DMF–ETHANOL–WATER REACTION MEDIUM

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Abstract. Mg-MOF-74 was prepared by a solvothermal route using magnesium nitrate hexahydrate and 2,5-dihydroxyterephthalic acid (H_4DOBDC). The initial Mg-to-ligand molar ratio was 3.3:1, and N,N-dimethylformamide (DMF), ethanol and distilled water were combined at a volume ratio of 15:1:1. The reaction mixture was treated in a sealed, PTFE-lined autoclave at 125 °C for 20 h, followed by washing, methanol solvent exchange, vacuum drying and activation. A yellow solid was recovered. Powder X-ray diffraction exhibited low-angle reflections compatible with Mg-MOF-74 formation. This thesis emphasizes the experimental sequence, the functions of post-synthetic treatment and the limits of the available structural evidence.

Keywords: Mg-MOF-74; solvothermal synthesis; magnesium nitrate; H_4DOBDC; solvent exchange; activation.

1. Introduction

Metal–organic frameworks (MOFs) are coordination solids constructed from metal-containing nodes and multifunctional organic linkers. Their ordered internal voids, diverse framework topologies and potentially accessible metal sites make them attractive for separation, gas capture and related applications. Within this family, MOF-74 structures feature channels extending through a framework built from divalent metal centers and 2,5-dihydroxyterephthalate-derived linkers. The magnesium

analogue, Mg-MOF-74 or CPO-27-Mg, is of interest because removal of coordinated molecules may expose metal sites to guest species [1, 2].

Obtaining an intended MOF phase requires control of solvent composition, precursor proportions, crystallization and activation. Reports on the MOF-74 family indicate that morphology and defect formation may depend on the synthesis environment [1, 3, 4]. A clearly reported protocol is therefore a prerequisite for evaluating subsequent material properties.

The aim of the present work was to prepare Mg-MOF-74 by a mixed-solvent solvothermal method and to describe the sequence from reagent dissolution to activation. Phase-related X-ray diffraction observations are considered only as initial corroboration of the targeted framework; an independent quantitative evaluation of yield, pore volume or adsorption capacity was not included in the source study.

2. Materials and Experimental Procedure

The inorganic precursor was magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$, and the organic component was 2,5-dihydroxyterephthalic acid, H_4DOBDC. The quantities charged were 1.85 mmol of magnesium salt and 0.56 mmol of ligand, corresponding to a nominal Mg:ligand molar ratio of approximately 3.3:1. The solvent system consisted of DMF, absolute ethanol and distilled water in a volumetric proportion of 15:1:1. These values refer to the reagent formulation reported for the experiment and should not be interpreted as an optimized recipe without comparative trials.

The solvent components were first combined. H_4DOBDC was introduced and mixed to distribute it through the medium; $Mg(NO_3)_2 \cdot 6H_2O$ was then added. Stirring was continued for 30 min to obtain a homogeneous reaction mixture suitable for solvothermal processing. The prepared mixture was transferred to a 200 mL autoclave equipped with a polytetrafluoroethylene (PTFE) liner. After sealing, the reactor was heated at 125 °C for 20 h.

At the end of the thermal period, the autoclave was allowed to cool naturally to ambient temperature. The yellow solid product was isolated by filtration. The precipitate was rinsed three times with fresh DMF to remove residual soluble components. The solid was subsequently immersed in methanol for three days, with periodic replacement of the liquid, to exchange solvent retained within the material. It was vacuum-dried at 80 °C and finally activated under vacuum at 220 °C for 12 h. The stated activation conditions describe the treatment applied to the recovered material; the extent of guest removal was not quantified.

3. Results and Discussion

The experimental sequence yielded a yellow solid following the 125 °C solvothermal treatment. This observation demonstrates formation and recovery of a solid product, but color alone cannot establish a unique crystalline phase. The investigation therefore also used powder X-ray diffraction on a SHIMADZU XRD-6100 instrument. Reflections near $2\theta=6.8°$ and within approximately 11.8–12.3° were reported and were interpreted as being consistent with the characteristic low-angle diffraction behavior of Mg-MOF-74. A more detailed interpretation of these observations is the focus of the companion thesis.

The procedure has three stages: contact between precursors in the mixed solvent, sealed-autoclave crystallization, and post-synthetic washing, solvent exchange and activation. These stages describe the functions of the treatments, rather than experimentally measured removal efficiencies. Removing retained molecules is important before future porosity measurements.

The Mg:ligand ratio is a reagent formulation, not a measured framework composition. No controlled variation of the 15:1:1 solvent ratio was reported. Previous studies describe the influence of processing conditions on MOF-74 crystal morphology [3] and the possibility of solvent-derived defects affecting adsorption [1]. Accordingly,

additional batches and complementary measurements would be needed to evaluate optimization or reproducibility.

Solvent exchange and activation are especially relevant to practical characterization. DMF used during synthesis may remain trapped in channels or associated with coordination sites; replacing it with methanol creates an additional opportunity to remove it before vacuum treatment. Nevertheless, an X-ray diffractogram by itself does not quantify residual DMF or methanol. Thermogravimetry and vibrational spectroscopy would be suitable complementary methods to assess solvent removal, while nitrogen sorption could establish whether the accessible pore structure had been preserved.

No numerical yield, particle-size distribution, BET surface area, adsorption isotherm or batch-to-batch study was reported. XRD thus offers preliminary structural evidence without establishing adsorption performance or quantitative phase purity. Complete-profile reference matching remains necessary.

4. Conclusion

A magnesium-based MOF product was obtained from $Mg(NO_3)_2 \cdot 6H_2O$ and H_4DOBDC using a DMF–ethanol–water reaction medium. The key conditions were Mg:ligand = 3.3:1, solvent volumes in the ratio 15:1:1, crystallization at 125 °C for 20 h, followed by DMF washing, three-day methanol exchange, vacuum drying at 80 °C and activation at 220 °C for 12 h. The observed diffraction features were compatible with Mg-MOF-74, while final phase identification and verification of accessible porosity require additional characterization. The procedure provides a reproducible starting description for future controlled synthesis studies.

References

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